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Optical and morphological characterization of polyacrylamide hydrogel and liquid crystal systems

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Abstract

In this work, the thermotropic liquid crystal MBBA (*N*-(4-methoxybenzilidene)-4-butylaniline), entrapped on hydrogels, based on cross-linked polyacrylamide (PAAm), was studied. The liquid crystalline phases of system were characterized by polarized optical microscopy (POM), refractive index, optical transmittance, scanning electron microscopy (SEM) and water loss. It was verified the presence of birefringence on hydrogel + liquid crystal. The dynamic of formation of such birefringence finished 40 days after the hydrogel synthesis. The effective birefringence Δn, i.e., the difference on refractive index of polyacrylamide hydrogel to refractive index of hydrogel + liquid crystal (Δn_1) and the difference on refractive index of liquid crystal (MBBA) to refractive index of hydrogel + liquid crystal (Δn_2) are dependent of content of acrylamide (AAm) and MBBA on hydrogel. The increase on Δn_1 and Δn_2 with the polyacrylamide content on hydrogel was attributed to decreasing of the mobility liquid crystal inside the hydrogel. Also, an increase on MBBA concentration in the polymeric matrix provides a reduction in the values of optical transmittance in the system. The morphology observed by SEM shows that hydrogel + liquid crystal is more compact that PAAm hydrogels. The presence of MBBA causes an increase in hydrophobicity. The water loss speed is favored by the increase in the amount of MBBA present in the hydrogels.

Keywords: Hydrogels; Thermotropic liquid crystal; PDLC confined systems

1. Introduction

At present, polymeric materials have been widely studied by several researchers from distinct areas, including biomedical and biotechnological [1,2] ones to explore further the potentials of these materials. The manifest interest in hydrogels derives from their characteristics, particularly biocompatibility and non-toxicity [3–7]. Hydrogels are materials formed by hydrophilic polymer networks that are capable of retaining a large amount of water [8–11]. Due to their satisfactory biocompatibility, hydrogels are potential candidates for application in the medical and pharmacological areas. Among their many applications, contact lenses,

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separation processes, drug carriers, cell culture substrates, therapeutical implants stand out [12–14]. Hydrogels are frequently synthesized by means of polymerization of acrylic monomers in isotropic solvents. This polymerization produces three-dimensionally cross-linked gels whose morphology is constituted by pores with randomly distributed size and filled with solvent, usually water [15].

Liquid crystals (LC) are substances that present mechanical characteristics of a liquid (fluidity) and optical characteristics of a crystal (optical anisotropy). Liquid crystals are classified as either thermotropic or lyotropic. Thermotropics are formed by the arrangement of individual molecules (pure substances) and lyotropic ones by micelles (amphiphilic molecules mixed with a solvent, usually water). The confinement of liquid crystals in polymeric matrices has raised a particular interest due to their technological applications. The best-known PDLC's (Polymer Dispersed Liquid Crystals) are used as displays and "switchable windows" [16–20]. Much work has been published on the subject. Kyu et al. [21] observed that the process of formation of textures with the temporal evolution of a given liquid crystal in a certain polymeric matrix involves competition between the liquid–liquid phases and the arrangement of mesophases of the liquid crystal within the matrix. Vaia et al. [22] reported that the type of polymerization involved in the liquid crystal confinement process in many penta-acrylate polymeric matrix is primordial for the control of the morphological structures formed. The literature also reports a large number of papers on thermodynamic separation of PDLC phases. Borrajo et al. [23] studied the separation of liquid crystals dispersed in epoxy resin through the Flory–Huggins theory (free mixture energy for isotropic phases) along with the Maier–Saupe theory (transition phase of nematic liquid crystal). Kihara et al. [24] demonstrated the effect of the composition and the nature of the LC copolymer side chain on the miscibility of blends constituted by low molar mass copolymer LC/LC. Blend phase transition was analyzed by DSC measurement and the textures obtained by polarized optical microscopy (POM). Bouchaour et al. [25] investigated the thermodynamic process involved in the construction of phase diagrams of the system formed by poly(2-phenoxy-ethyl-acrylate) and thermotropic liquid crystal LMWLC (4-ciano-4′ *n*-pentil-biphenyl or 5CB) by POM and DSC.

Another form of confinement of liquid crystals consists in introducing them into hydrogels, which results in distinct properties [26–29] from those of the pure components. In this work, crystalline liquid phases of polyacrylamide hydrogels (PAAm) together with thermotropic liquid crystal MBBA (*N*-(4-methoxybenzilidene)-4-butylaniline) were investigated. The liquid-crystalline system phases (hydrogel + liquid crystal) were characterized by refractometry, polarized optical microscopy (POM), optical transmittance, scanning electron microscopy (SEM) and measures of water loss.

2. Experimental

2.1. Hydrogels synthesis

Hydrogels were synthesized in a sealed environment by radicalar photochemical polymerization of acrylamide monomer, AAm (Aldrich, 14,866-5) in the presence of *N*,*N*′-methylene-bis-acrylamide, MBAAm, (Plusone, 17-1304-02) as a cross-linking agent. Potassium periodate, KIO_4, (Vetec, 700), was used as a photopolymerization indicator. The thermotropic liquid crystal *N*-(4-methoxybenzilidene)-4-(butylaniline), MBBA (Riedel-De Haën Ag, 36320) was used. The AAm, MBAAm, and MBBA concentrations used in synthesis are given in Table 1. In synthesis, AAm monomer was added with the cross-linking agent MBAAm, and the liquid crystal MBBA to an aqueous solution of KIO_4 (5.0 μmol mL^{-1}). The resulting solution was placed between two glass plates measuring $76 \times 26 \times 1.1$ (in mm) with a spacer 1.0 mm thick and the plates were exposed to Hg vapor light ($\lambda = 254$–580 nm) for 40 min. For characterization, the polymeric membranes were labeled according to the notation (*X*-*Y*-*Z*), where *X* is the molar concentration of AAm, *Y* is the % molar concentration of MBAAm in relation to AAm and *Z* the amount (% v/v) of MBBA.

Table 1
AAm, MBAAm, and MBBA concentrations in feed solution used in the synthesis of hydrogels (2-1-Z), (3.5-1-Z), (5-1-Z), and (10-1-Z)

	AAm (μmol mL^{-1})	MBAAm (μmol mL^{-1})	MBBA (v/v %)
Hydrogel 2-1-Z			
(2-1-0)	2000	20	0
(2-1-1.0)	2000	20	1.0
(2-1-2.5)	2000	20	2.5
Hydrogel 3.5-1-Z			
(3.5-1-0)	3500	35	0
(3.5-1-1.0)	3500	35	1.0
(3.5-1-2.5)	3500	35	2.5
Hydrogel 5-1-Z			
(5-1-0)	5000	50	0
(5-1-1.0)	5000	50	1.0
(5-1-2.5)	5000	50	2.5
Hydrogel 10-1-Z			
(10-1-0)	10000	100	0
(10-1-1.0)	10000	100	1.0
(10-1-2.5)	10000	100	2.5

2.2. Polarized optical microscopy

Polarized optical microscopy (POM) is an important technique in the study of liquid crystalline mesophases and the transition temperature of liquid crystals. The microscope used in this work (DM—LP Leica with CCD—DXC—107A Sony camera attached) has a polarizer at the base and an analyzer at 90° above the objective lens. The sample is placed between the two polarizers. When light passes through the sample, it suffers modifications in its polarization plane due to the optical anisotropy of the material, which in turn reveals the typical textures of each phase.

In this work, the textures were obtained at room temperature (~25.0 °C) at different platinum rotation angles: 0°, 22.5°, 45°, 67.5°, and 90°. In this way, it was possible to observe the appearance of sample birefringence.

2.3. Refractometry

An ABBE refractometer model 3T-Atago was used to measure the refraction index. The refractometer possesses scale complete, ranging over the entire refraction index from 1.300 to 1.700 with an accuracy of 0.001 and BRIX 0–95% with a precision of 0.2%. The refractometer also has a top prism lightning feature which enables analyzing opaque substances and thermostatization, which allows reading at a single temperature and also measurements at different temperatures. In this work, the analysis temperature range used was from 12.0 to 46.0 °C. Thus, it was possible to observe the refraction index of the hydrogels as a function of temperature.

2.4. Optical transmittance

Optical transmittance measurements of hydrogels with thermotropic confined liquid crystal were carried out at room temperature (~25.0 °C) using a UV–visible spectrophotometer Cary 50 Conc with reading range from 200 to 1100 nm. This spectrophotometer has an optional device (sample holder) that allows measuring solid materials such as hydrogels. To perform the measurements, the hydrogels were cut to 2.0×2.0 (in cm), placed between two glass plates and into the sample holder. Transmittance spectrum was obtained as a function of wavelength for the entire visible region.

2.5. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to analyze surface morphological properties of hydrogels with and without confined liquid crystal. The samples were frozen in liquid nitrogen for analysis. Afterwards, the samples were lyophilized using the apparatus Christ Gefriertrocknungsanlagen. Lyophilization lasted 24 h and the temperature was kept at −55 °C. Hydrogel micrographs were obtained using a scanning electron microscope Shimadzu, model SS-550 Superscan.

2.6. Loss of water

Firstly, the mass of water-soaked hydrogel was determined. Next, the hydrogel was removed from water and kept in an oven at 25.0 °C. In the first 10 h, the variation of the hydrogel mass was followed up every 30 min. After this period, the hydrogel mass was measured in larger intervals (6 h). The values of hydrogel water loss were obtained through Eq. (1):

$$\text{Water loss } (\%) = [(M_Q - M_t) \times (M_Q)^{-1}] \times 100 \qquad (1)$$

where M_Q and M_t are the soaked hydrogel mass in equilibrium and hydrogel mass after a "t" time, respectively.

3. Results and discussion

The evolution of birefringence of hydrogels with time was based on textures obtained by POM. It was observed that hydrogel samples containing liquid crystals present birefringence and that it stabilizes 40 days after

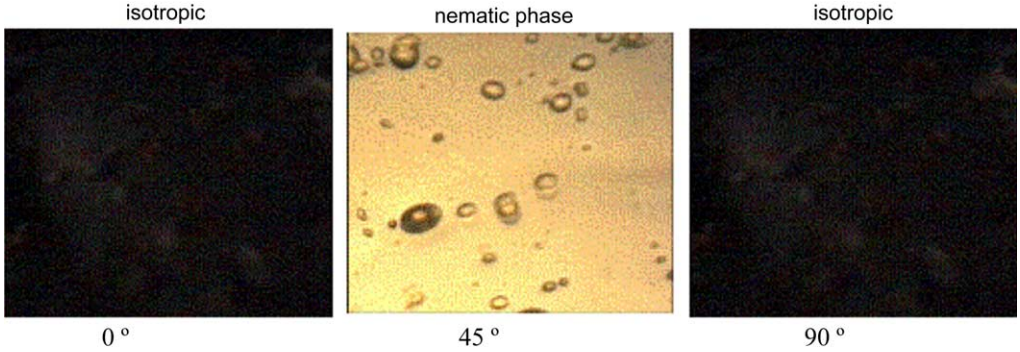

Fig. 1. Optical micrographs of sample (5-1-1.0) obtained 20 days after hydrogel synthesis at several polarization angles. Textures of the sample between crossed polarisers.

synthesis. Fig. 1 presents optical micrographs of hydrogel (5-1-1.0) at three polarization angles, 20 days after the preparation of the material. It can be observed the texture and birefringence of the hydrogel with liquid crystal confined. Fig. 2 shows optical micrographs of the system (5-1-1.0) 40 days after synthesis. Fig. 3 shows optical micrographs of the system (5-1-0), in which the texture of hydrogel without liquid crystal can be barely observed.

Comparison of systems with confined MBBA (Figs. 1 and 2) and hydrogel matrix without MBBA (Fig. 3) reveals that samples with liquid crystal MBBA confined in polymeric matrix presents birefringence (optical anisotropy). The textures observed on the samples without liquid crystal are typical of isotropic systems, whose optical anisotropy is null. Thus, the birefringence presented by hydrogel MBBA systems (Figs. 1 and 2) can be attributed exclusively to the presence of the liquid crystal. It was also observed that birefringence becomes stable 40 days after sample synthesis.

Through n measurements, using the ABBE Refractometer, it was possible to determine the effective birefringence of the systems studied (Δn). To determine Δn, two distinct methods were used: the first corresponds to the difference between the refraction indexes of hydrogel with MBBA (n_{HLC}) and hydrogel without MBBA (n_H), hence called Δn_1 ($\Delta n_1 = n_H - n_{HLC}$), represented in Fig. 4. In the second method, Fig. 5, effective

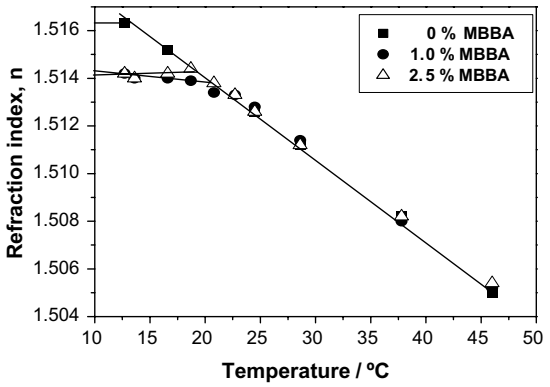

Fig. 4. Dependence between refraction index and temperature for system (3.5-1-Z).

birefringence was determined through the difference of the refraction indexes of the liquid crystal (n_{LC}) and the refraction indexes of hydrogels containing MBBA (n_{HLC}), hence called Δn_2 ($\Delta n_2 = n_{LC} - n_{HLC}$).

For samples with 1.0 v:v-% MBBA conc., the values of Δn_1 ($\times 10^4$) were 17.2, 18.2, and 17.8, and the values of Δn_2 ($\times 10^4$) were 18.3, 20.8, and 22.6, for AAm concentrations of 2000, 3500, and 5000 μmol mL^{-1}, respectively. For systems with 2.5 v:v-% MBBA, the values of Δn_1 ($\times 10^4$) were 20.3, 22.1, and 25.9, and the values

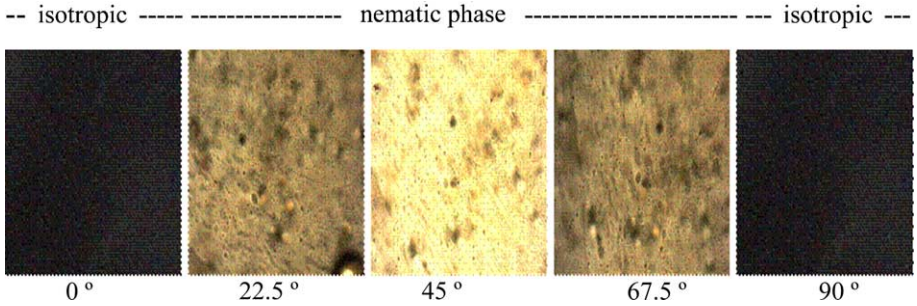

Fig. 2. Optical micrographs of sample (5-1-1.0) obtained 40 days after hydrogel synthesis at several polarization angles. Textures of the sample between crossed polarisers.

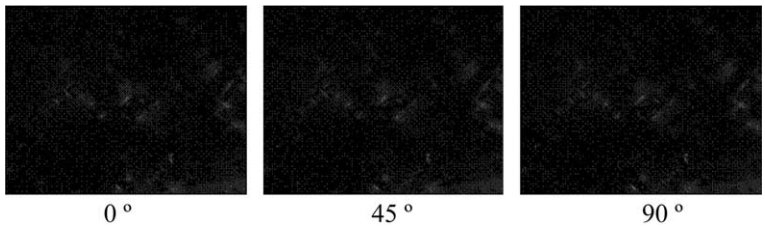

Fig. 3. Optical micrographs of sample (5-1-0) obtained 40 days after hydrogel synthesis at several polarization angles. Textures of the sample between crossed polarisers.

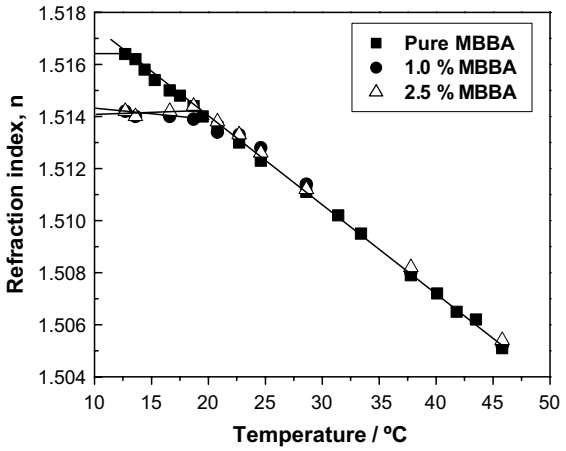

Fig. 5. Dependence between refraction index and temperature for MBBA and system (3.5-1-Z).

of Δn_2 ($\times 10^4$) were 22.3, 25.0 and 29.6, for the above-mentioned AAm concentrations.

Fig. 6 shows the dependence between the values of Δn_1 and Δn_2 the concentration of AAm in the hydrogel. The analysis of Fig. 6 reveals that Δn increases in both methods with the increase in the concentration of AAm. Thus, the first increase in Δn can be attributed to the increase in the quantity of polymer in the sample, as the increase in the concentration of acrylamide makes the matrix more compact and reduces the mobility of the polyacrylamide chains. For Δn_2, the same effect is observed, however with a greater intensity than that of Δn_1. It is also observed that for both methods (Δn_1 and Δn_2), the largest effective values of Δn are obtained with 2.5 v:v-% liquid crystal.

It can be observed in Fig. 7 that the refraction index of species (3.5-1-0) and MBBA decrease linearly with temperature.

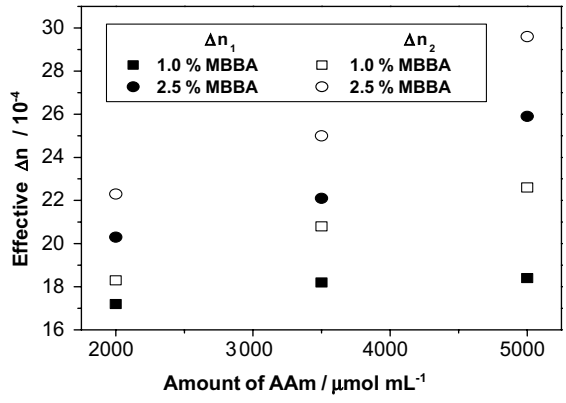

Fig. 6. Dependence between effective Δn and polyacrylamide concentration for hydrogel + MBBA systems.

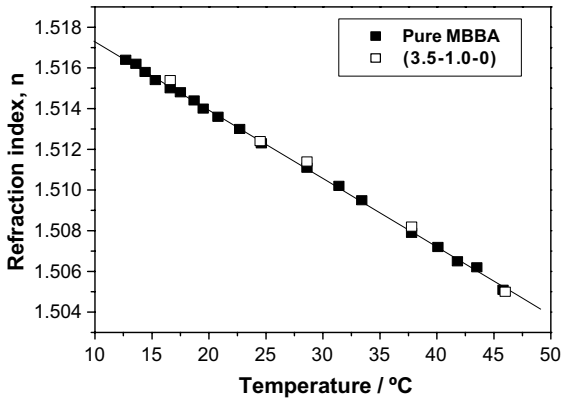

Fig. 7. Refraction index of hydrogel (3.5-1-0) and MBBA as a function of temperature.

In contrast, when the liquid crystal is confined into the polymeric matrix, two distinct behaviors are observed, Figs. 4 and 5. In the temperature range of 12–20 °C, the refraction index remains constant. Over 20 °C, the refraction index of all samples decreases linearly with temperature. This change in the behavior of Δn is related to the phase transition of the thermotropic liquid crystal MBBA (crystalline → nematic), which occurs around 21 °C [30]. When the thermotropic MBBA liquid crystal is confined in hydrogel, it probably interacts with the PAAm matrix. At temperatures lower than 20 °C, MBBA is in the crystalline phase, and therefore its molecules are organized (low entropy). If a small amount of energy is supplied to the system so that the temperature does not rise above 20 °C, part of this energy would be consumed by the MBBA molecules, which would assume conformations different from the initial ones. Therefore, the energy supplied would not be enough to undo such interactions. In contrast, when enough energy is supplied to the system so that its temperature rises above 20 °C, the MBBA–PAAm interactions are no longer favored, and the properties of the hydrogel + liquid crystal molecules, such as the refraction index, become closer to individual values.

The samples were also characterized using optical transmittance measurements. Fig. 8 shows optical transmittance spectra in the 350–800 nm range for system (X-1-1.0).

It can be observed that for pure polyacrylamide hydrogel, optical transmittance practically remained unaltered in the whole visible region. The value of transmittance for this system remains between 90% and 100%, indicating that practically all light is transmitted through the sample as the hydrogels are practically made up of water. Higher transmittance values are obtained for systems type (2-1-1.0), whose cross-linking density is the lowest in relation to the others. As the polymeric matrix becomes denser due to the increase

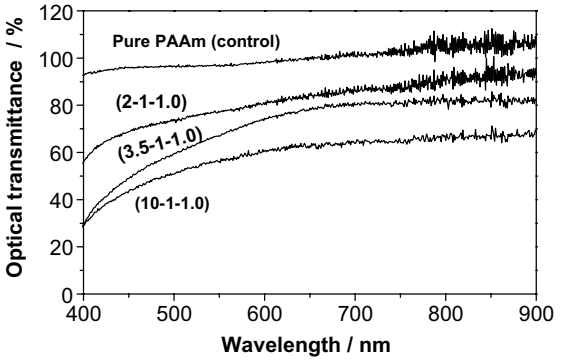

Fig. 8. Dependence between optical transmittance and wavelength for system (X-1-1.0).

in the concentration of acrylamide in the hydrogels, there is a sizable decrease in optical transmittance, which is attributed to the loss of mobility of the liquid crystal in the polymeric matrix. Fig. 9 shows the visible region

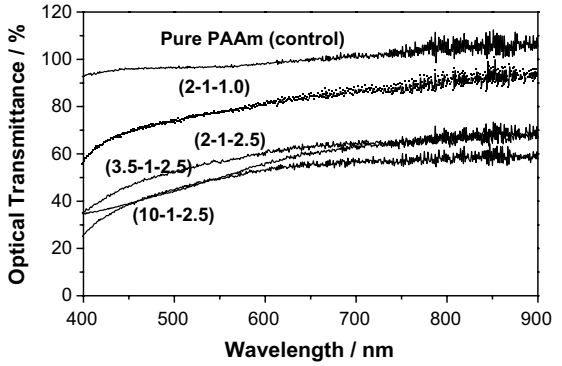

Fig. 9. Dependence between optical transmittance and wavelength for system (X-1-2.5).

transmittance spectra of systems (X-1-2.5). For system (2-1-X), it was observed that transmittance decreases with the increase in the confinement of the liquid crystals in the polyacrylamide hydrogels. This is due to the absorption of the liquid crystal in the visible range.

One can also observe a behavior identical to that of system (X-1-1.0). Nevertheless, it is not observed a marked decrease in optical transmittance with the increase in acrylamide concentration, i.e., the transmittance of the system (3.5-1-2.5) is nearly equal to that of system (2-1-2.5). Thus, when MBBA is present in larger concentrations (2.5 v:v-%) in the polymeric matrix, the increase in the density of the polymeric matrix does not lead to a decrease in the system transmittance, i.e., the major factor for this decrease in this system is the presence of the liquid crystal rather than acrylamide concentration.

Fig. 10a shows electronic micrographs of the surface of pure polyacrylamide hydrogel and Fig. 10b shows the surface of the polyacrylamide hydrogel with confined MBBA.

It can be observed in the micrographs that pure PAAm hydrogel has a porous surface. The analysis of the electronic micrographs of MBBA inclusion hydrogels (Fig. 10b) reveals the pores are filled, which makes the matrix more compact in relation to the pure polyacrylamide matrix.

Fig. 11a and b presents electronic micrographs of the polyacrylamide matrix with confined MBBA further enlarged. Through the analysis of these micrographs, one can see that the surface of the hydrogels with confined MBBA presents well-organized structures distributed around the membrane pores, thus contributing for its compaction.

Water loss measurements were carried out to demonstrate the compaction of the matrix of the systems studied. Fig. 12 shows water loss curves of pure PAAm hydrogels (5-1-0), and 1.0 and 2.5 % confined MBBA

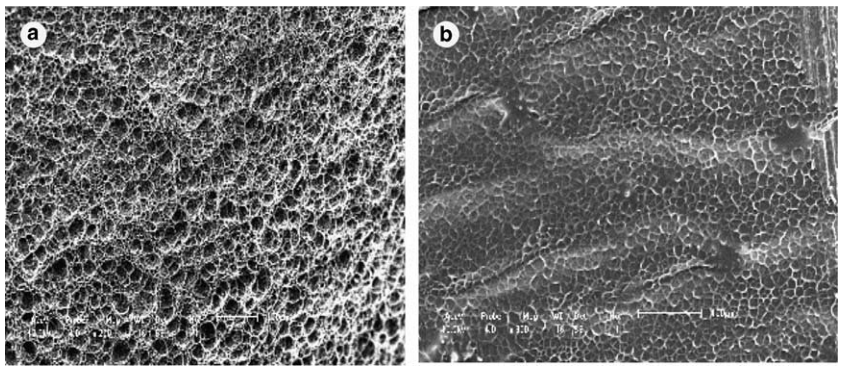

Fig. 10. SEM micrographs of the surface of hydrogels lyophilized at 25 °C. ((a): PAAm, Magnification: 200×; (b): PAAm with confined MBBA, Magnification: 300×).

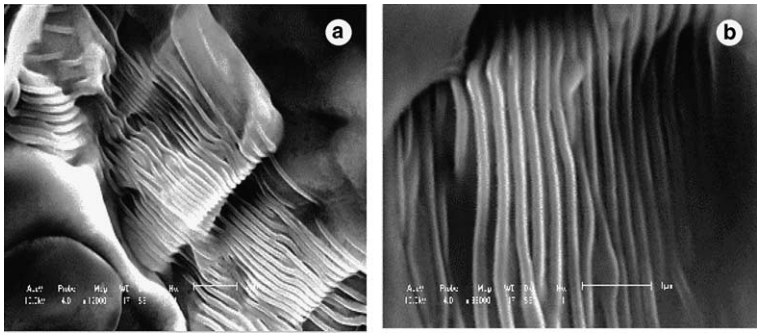

Fig. 11. SEM micrographs of the surface of PAAm hydrogels with MBBA lyophilized at 25.0 °C. ((a), Magnification: 12,000×; (b), Magnification: 36,000×).

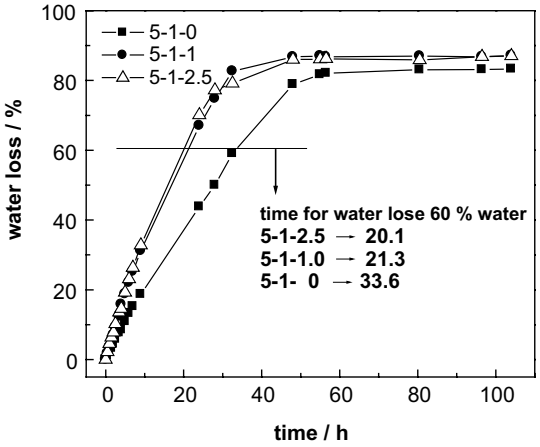

Fig. 12. Water loss curves of pure PAAm hydrogels (5.0-1-0), and 1.0 and 2.5 v:v-% confined MBBA hydrogels at 25.0 °C.

hydrogels. Fig. 12 reveals that water loss occurs more rapidly in hydrogels with liquid crystal than otherwise due to its presence in the matrix structure, which renders the matrix more hydrophobic. Examining hydrogel (5-1-0), we observe that it loses 60% water in approximately 33 h. System (5-1-1.0) takes approximately 21 h to loose the same amount of water, while system (5-1-2.5) takes about 20 h. Therefore, we can see that water loss is favored by the increase in the amount of MBBA present in the hydrogels.

4. Conclusions

Optical microscopy and refractometry results indicate that the system made up of polyacrylamide hydrogel + liquid crystal (MBBA) has a characteristic dynamic arrangement. POM revealed that the birefringence presented by hydrogel + liquid crystal systems is exclusively due to the presence of MBBA in the polymeric matrix.

Refractometry data demonstrate changes in the effective refraction index (n) of the system made up of hydrogels + MBBA in comparison to the characteristic n values of pure systems (MBBA and polyacrylamide hydrogels). POM revealed that the birefringence presented by the hydrogel + liquid crystal systems is exclusively due to the presence of MBBA in the polymeric matrix.

Optical transmittance measurements of hydrogel + liquid crystal systems demonstrate that the MBBA concentration in the polymeric matrix of system (2-1-Z) leads to a decrease in the optical transmittance values of the system. For systems type (X-1-1.0), an increase in polyacrylamide concentration (increase in crosslinking density) results in a decrease in optical transmittance due to the loss of mobility of the liquid crystal in the polymeric matrix. The decrease in optical transmittance of system (X-1-2.5) is no longer observed when the concentration of acrylamide is increased. It can be concluded that the major factor for the decrease of the optical transmittance of system (X-1-2.5) is the presence of the liquid crystal rather than the concentration of acrylamide.

SEM micrographs show that the hydrogels with confined MBBA present well-organized structures randomly distributed around the polymeric matrix pores, and that these structures contribute for compaction of hydrogels. Such compaction was confirmed through measurement of water loss by the matrix. It could be observed that the water loss speed is favored by the increase in the amount of MBBA present in the hydrogels. In conclusion, the presence of MBBA makes the matrix more hydrophobic.

Acknowledgements

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